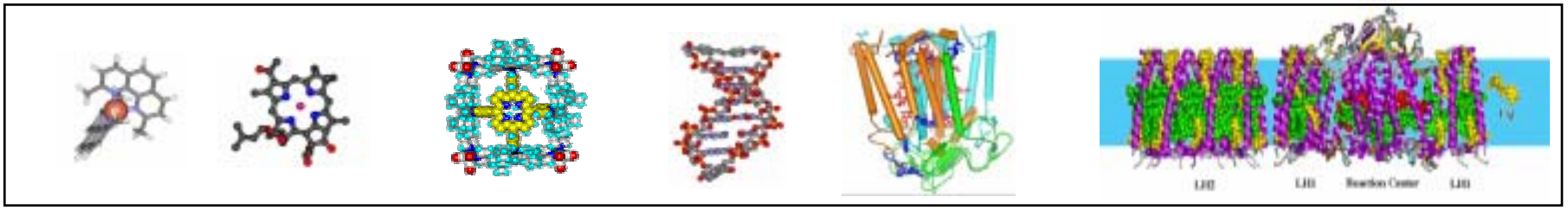
RESOLVING STRUTURE AND STRUCTURAL DYNAMICS OF DESIGNED PHOTOSYNTHETIC ARCHITECTURES



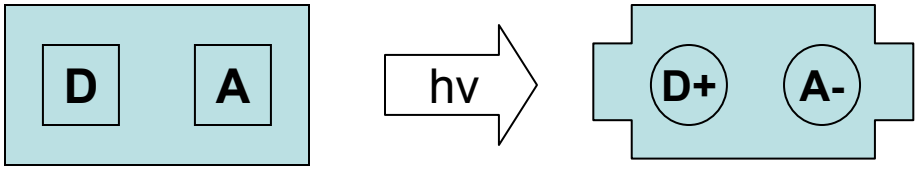
David M. Tiede[1], Lin X. Chen[1], Tijana Rajh[1], Xiaobing Zuo[1], Ruitian Zhang[1], Lianhe Yu[2], Jonathan S. Lindsey[2], Jodi O'Donnell[3], Joseph Hupp[3], and Frederick Lewis[3]

[1]Chemistry Division, Argonne National Laboratory, Argonne, IL 60439,
[2]Department of Chemistry, North Carolina State University, Raleigh, NC 27695, and
[3]Department of Chemistry, Northwestern University, Evanston, IL 60208

Workshop on Time Domain Science
Using X-ray Techniques
The Abby
Lake Geneva, Wisconsin
August 29th – September 1st 2004

Argonne Photosynthesis Group

Research Goal:
Light-induced Structural Dynamics
in Natural and Bio-mimetic Photosynthesis



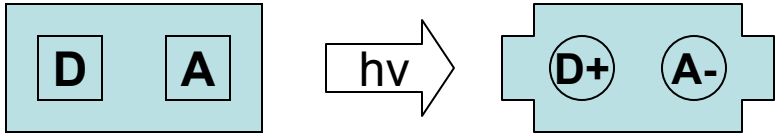
Critical Parameters
Structure/Structural Dynamics Linked to Photochemistry:

- Donor-acceptor/cofactors
- Solvent/matrix
- Atomic re-organization linked to ET(λ)
- Relaxation events (energy conversion)

Fundamental for understanding ET and energy conversion

Argonne Photosynthesis Group

Light-induced Structural Dynamics in Natural and Bio-mimetic Photosynthesis

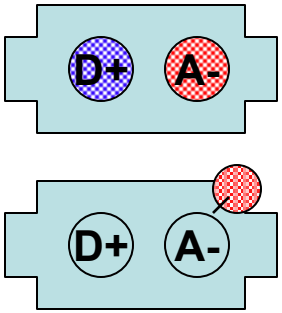


Approach

Resolution range

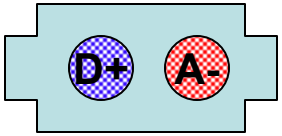
- Pulsed, multi-frequency EPR and associated techniques (ENDOR)
- EPR Spin-Probe Techniques
  - *Marion Thurnauer*
  - Oleg Poluektov
  - Lisa Utschig

- Cofactor and adjacent local-site structures
- Long-range coupling to local-site probes



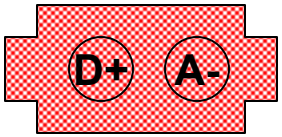
- Time-resolved synchrotron techniques
- X-ray spectroscopy (XAFS, XANES)
- fs Transient Optical Techniques
  - Lin Chen

- Excited-state photochemistry/structure
- Metal-centered Chromophores/co-factors



- Time-resolved X-ray scattering
- Molecular diffraction
  - D. Tiede

- Global structure
- Conformational ensembles
- Solvent interface

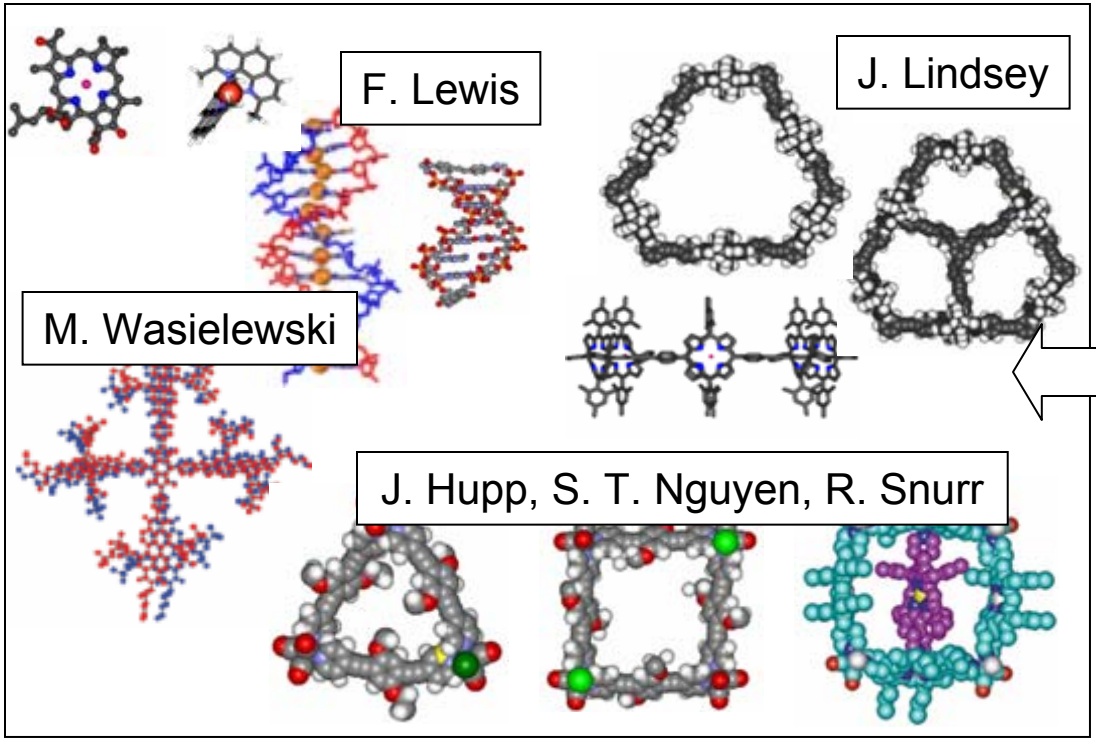


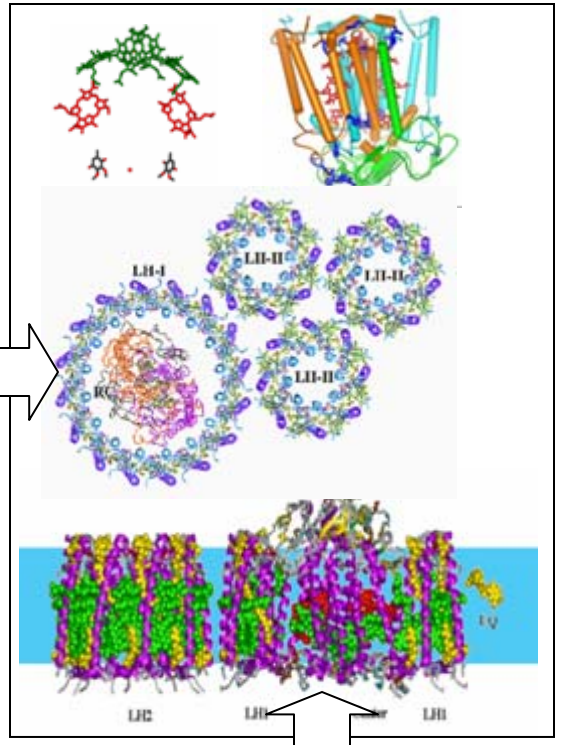
Supramolecular Photochemical Architectures:

Synthetic Photochemical Architectures

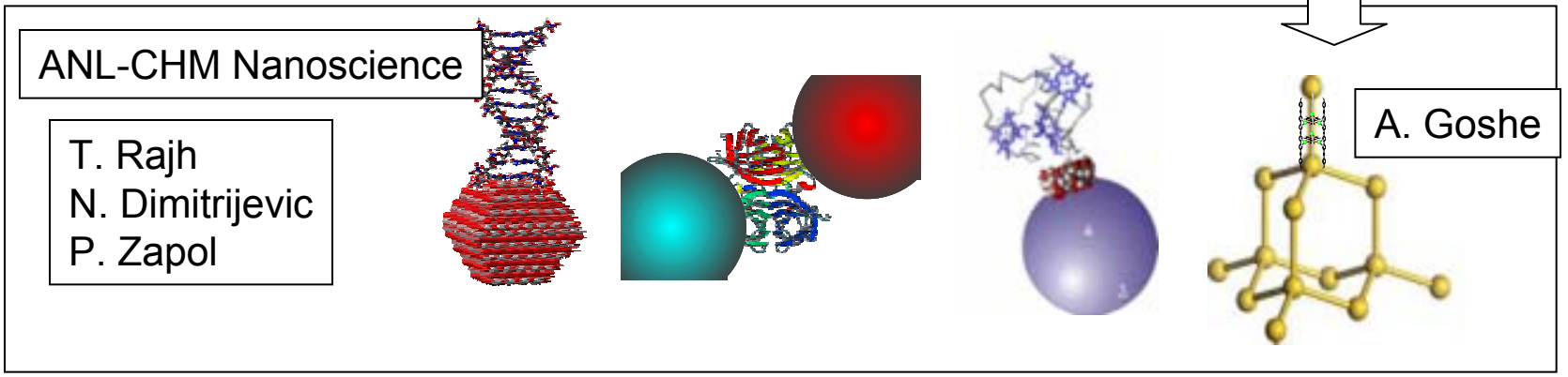
Biological Photosynthesis

Supra-molecular Chemistry





Nanoscale Hybrid Architectures



Direct Methods For Supramolecular Structure and ET-Linked Structure Change in Liquids:

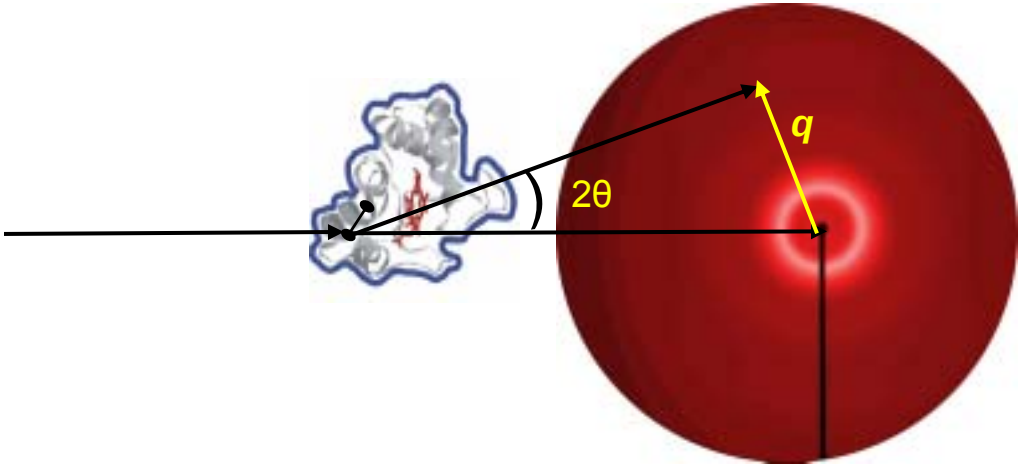
- **Crystallography**
- **NMR**
- **Molecular Dynamics**

New Approach:

Molecular Diffraction in Solution

- Generally Applicable
  - *inorganic, organic, biological*
- Direct, Quantitative: Correlate to Coordinate Models
  - *distinguish Crystal, NMR, MD models*
- High Time-resolution
  - *~ 100 ps current (3rd generation) synchrotron*
  - *< 100 fs 4th generation light source*

Coordinate-based X-ray Scattering: Orientationally-averaged Interference From All Atom Pairs



$q = (4\pi/\lambda)\sin(\theta)$

Calculate from crystallographic atomic form factors:

$$I(q) = \left\langle A(\mathbf{q})A(\mathbf{q})^{*} \right\rangle = \sum_{j}\sum_{k} f_j(q) f_k(q) \frac{\sin qr_{jk}}{qr_{jk}}$$

Debye equation

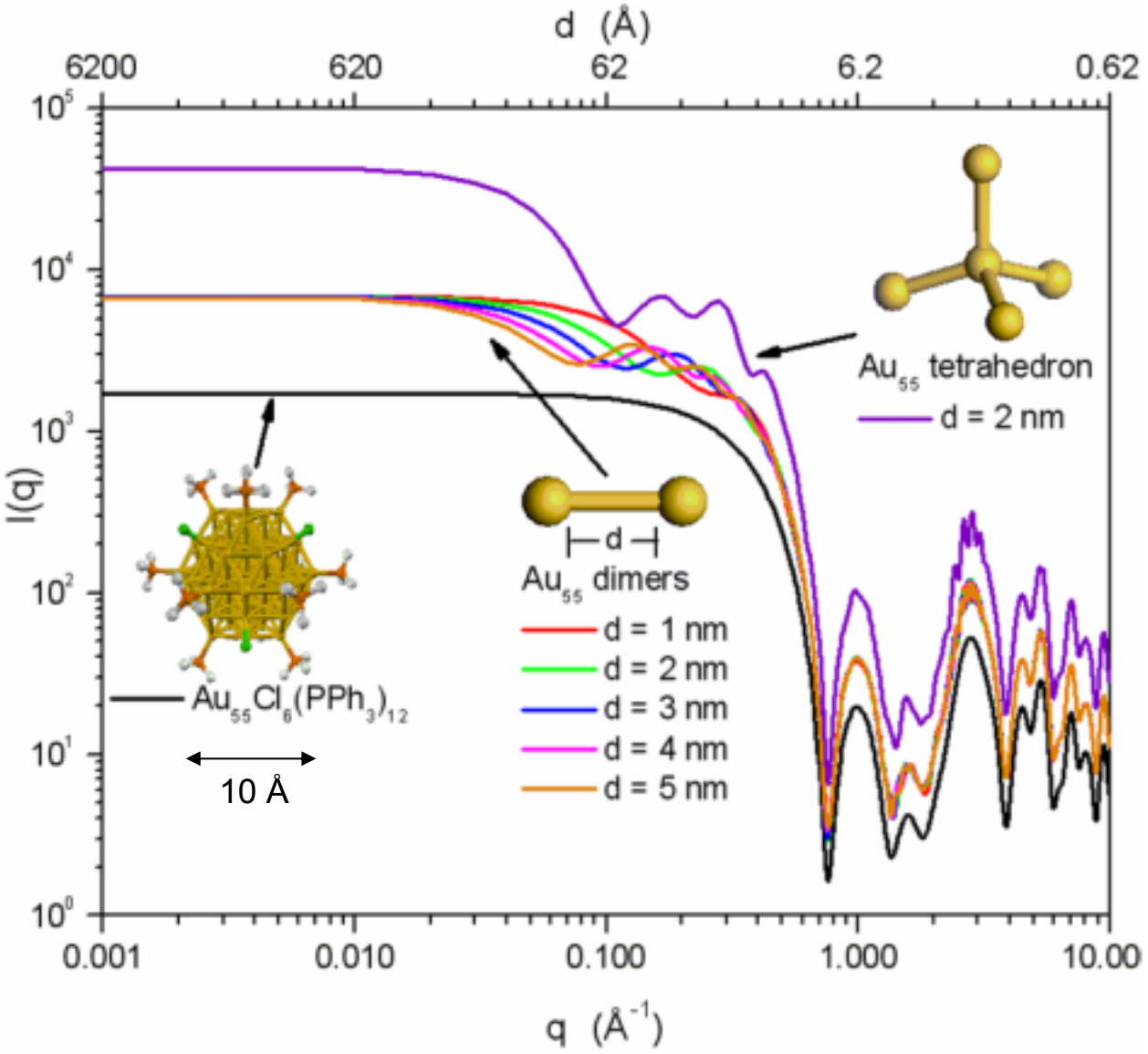
$$f(q) = \iiint dV \cdot \rho(\mathbf{r}) e^{-i\,\mathbf{qr}}$$

$$I(q) = \int p(r) \frac{\sin qr}{qr} dr$$

Scattering = FT (Pair distance distribution function)

Simulated Scattering for Au_{55} Architectures

Andrew Goshe



Au_{55} supramolecular dimensions (d ~ 10 Å)

X-ray Scattering of Mono-disperse systems reveals:

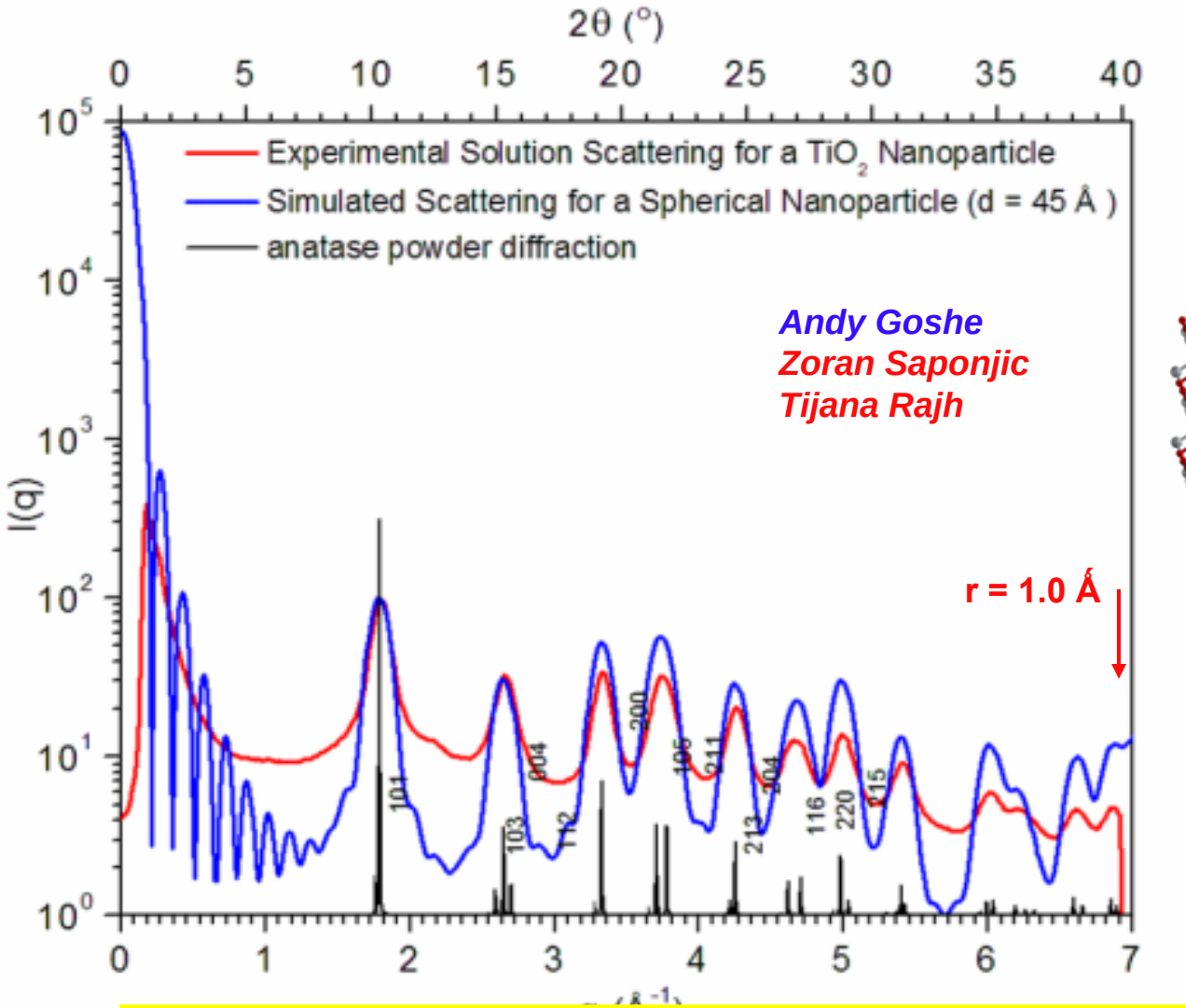
- size

- shape

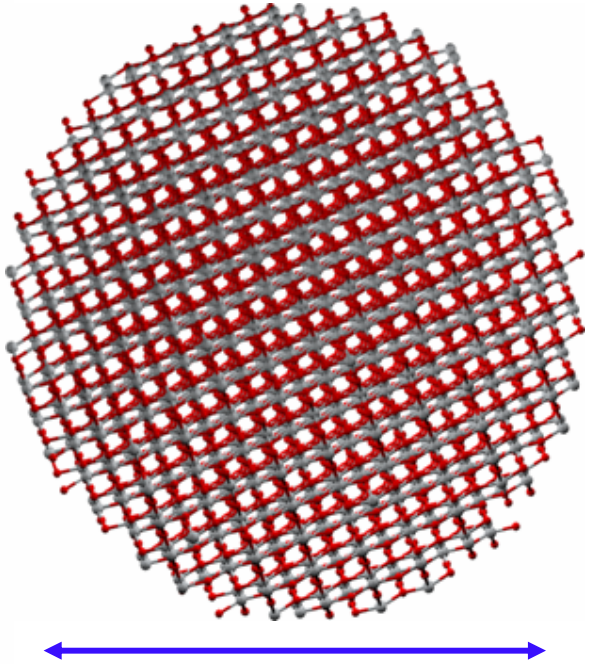
-internal structure of particles

-interparticle relationships

X-ray Scattering TiO_2 Nanoparticle (*supramolecular dimensions*) in Liquids



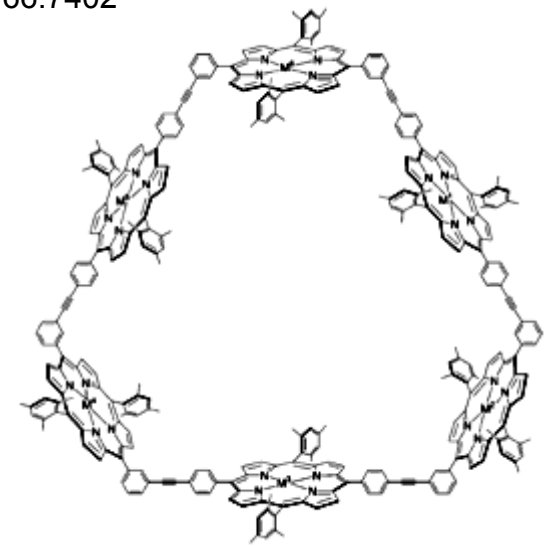
Anatase Nanoparticle

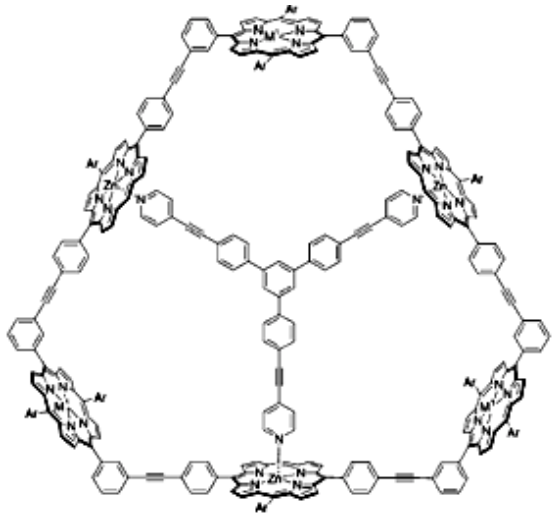


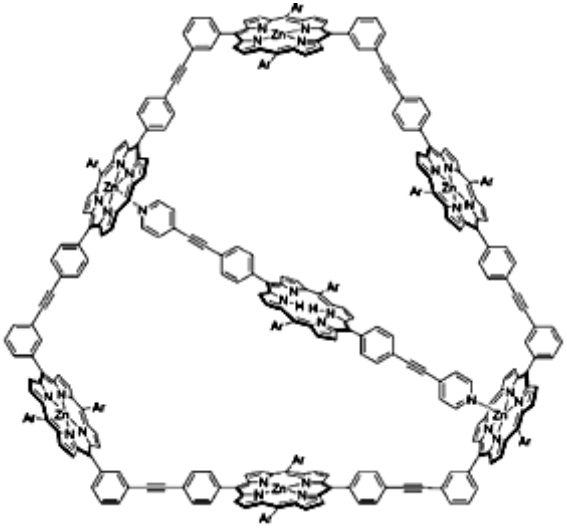
Experimental pattern reveals internal crystalline structure for nanoparticle, What about comparable experiments with molecules?

One Set of Lindsey Compounds:
Diphenylethyne Linked Multimeric Porphyrin Arrays

Yu, L. and Lindsey, J.S. (2001) J. Org. Chem. 66:7402

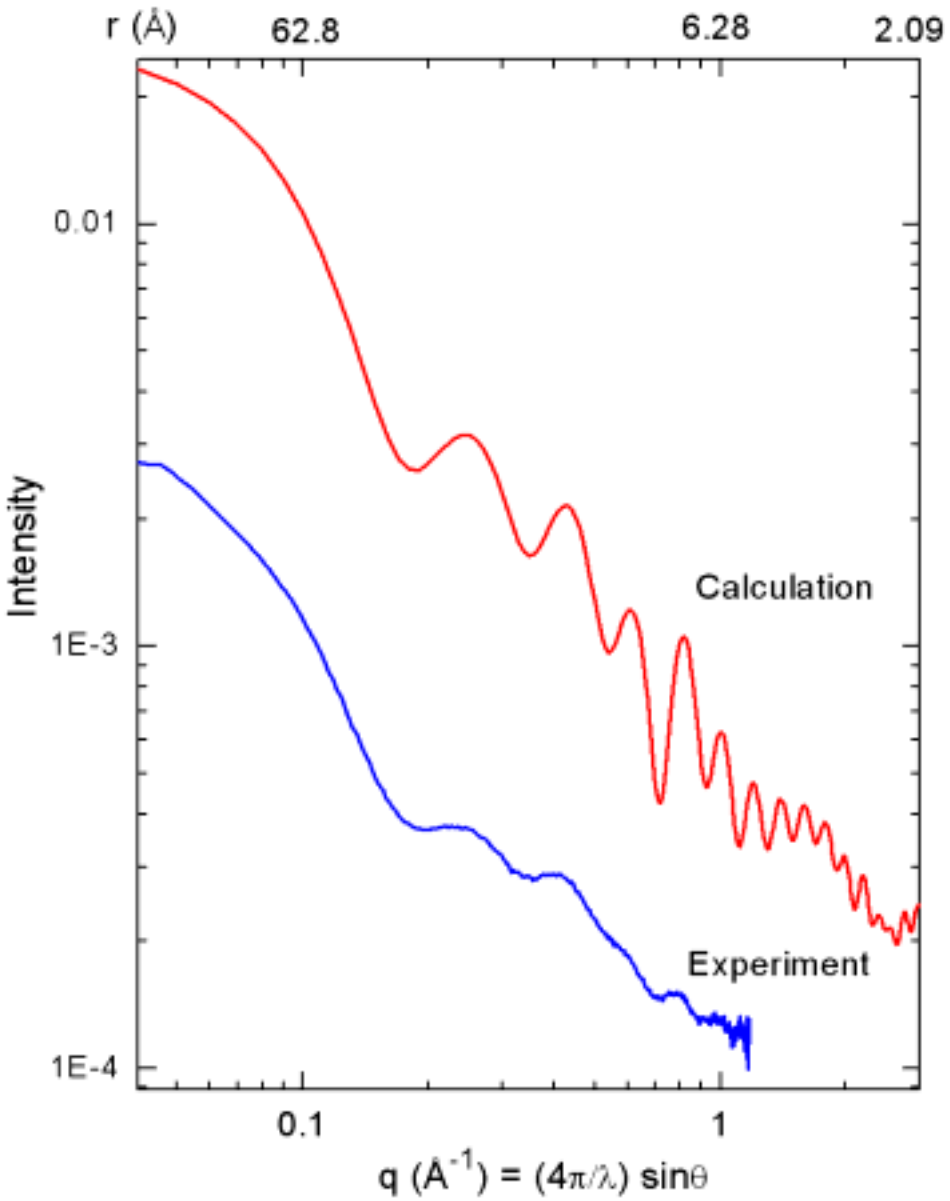


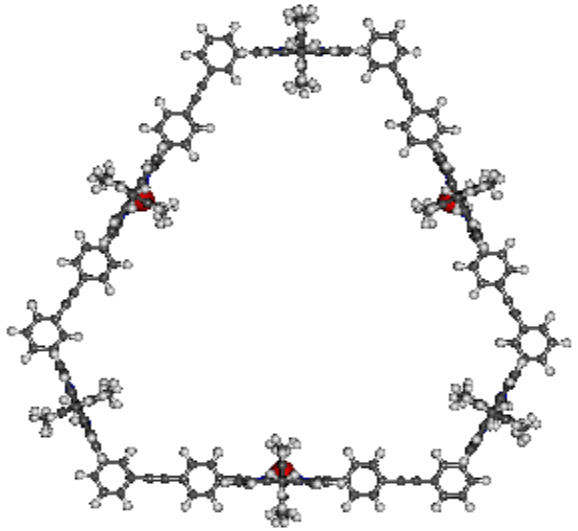




- **Models for Light-harvesting**
- **Building blocks**
  - > artificial photosynthesis
  - > sensors
  - > catalysis
- **Structure not determined**

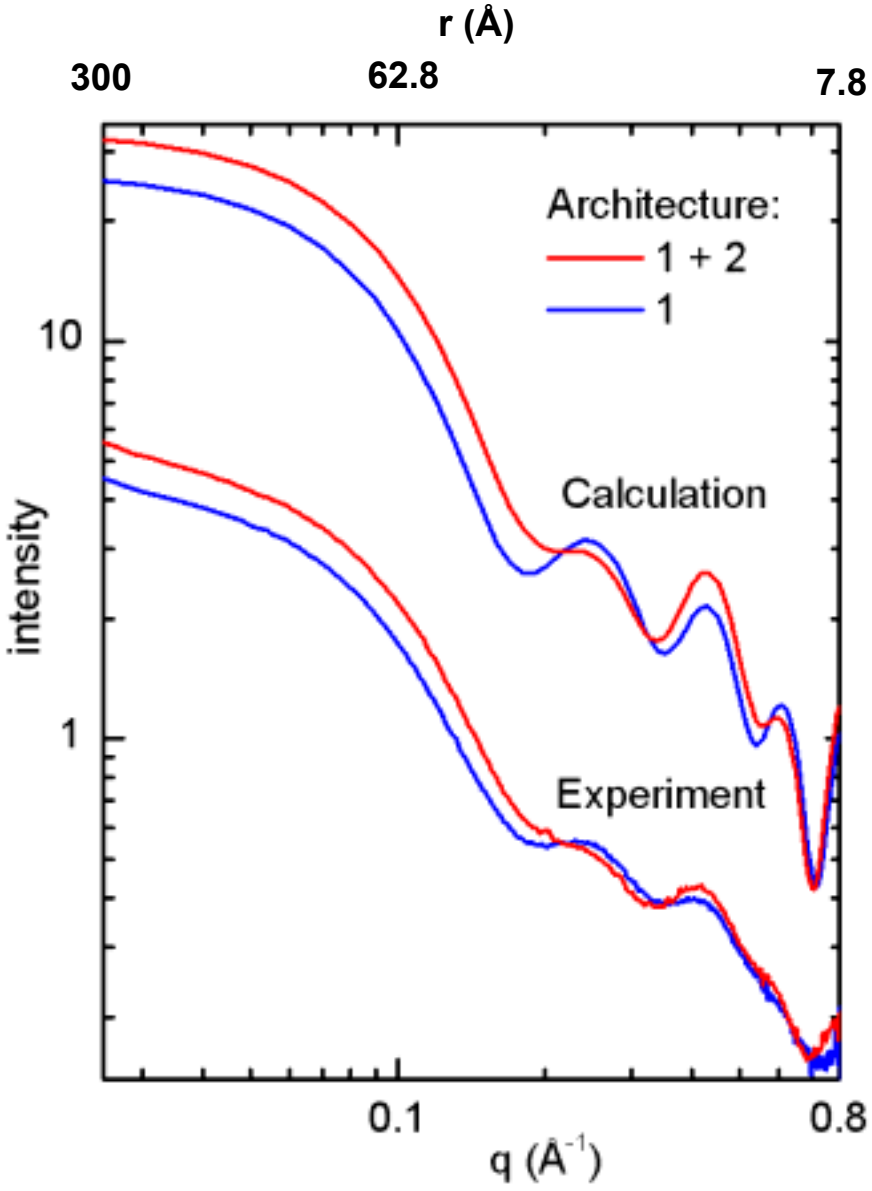
Scattering & Solution Diffraction for Porphyrin Wheel Architecture

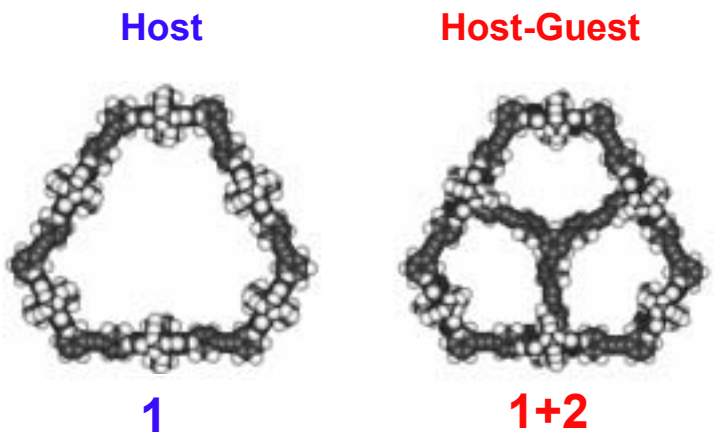




- Calculation:
  - Scattering
  - Interference = molecular diffraction (due to internal structure)
- Experiment (in toluene):
  - Scattering
  - Molecular diffraction (peak shifts, damped amplitudes)

Cyclic Porphyrin Hexamer Assemblies



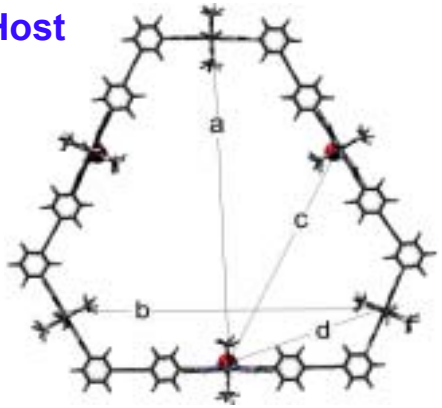


- **Measured Scattering for Porphyrin Assembly in Toluene to 4.5 Å Resolution (shown 7.8 Å resolution)**
- **Guest-Host Scattering *Generally* Consistent With Designed Structure**
- **Differences (Exp vs Model) Give Info on Molecular Structure**

PDF Analysis Porphyrin Wheel Architectures

Energy Minimized Models
(Lin Chen)

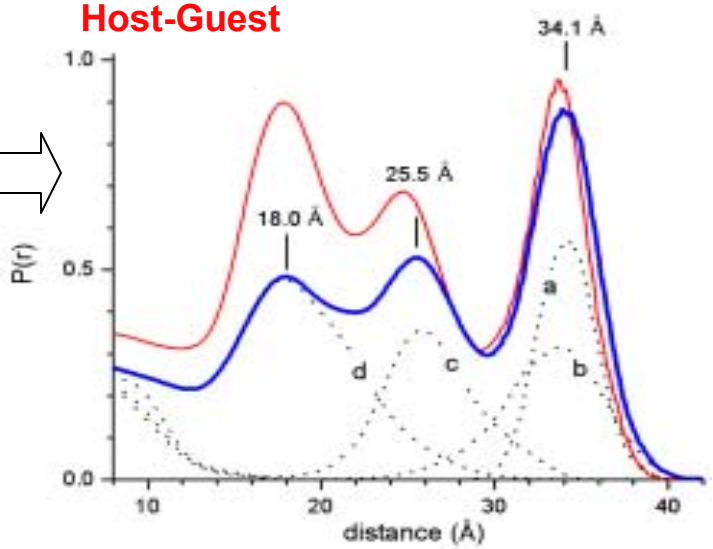
Host



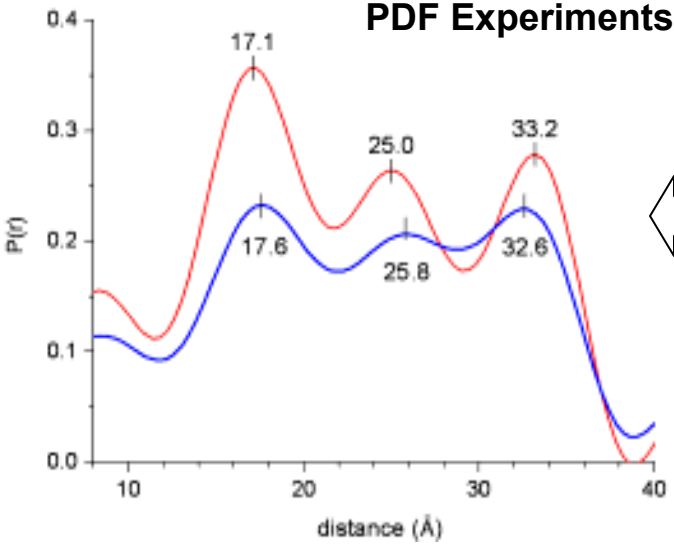
Host-Guest

PDF Models

Host
Host-Guest

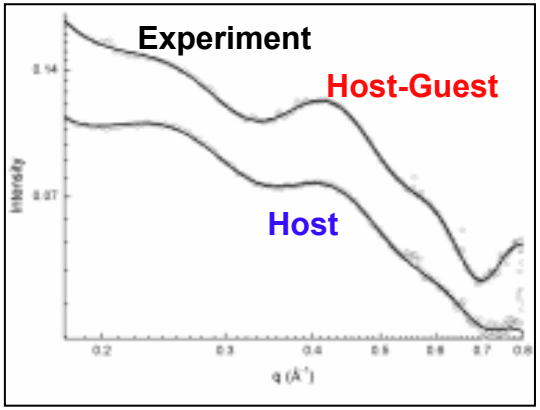


PDF Experiments



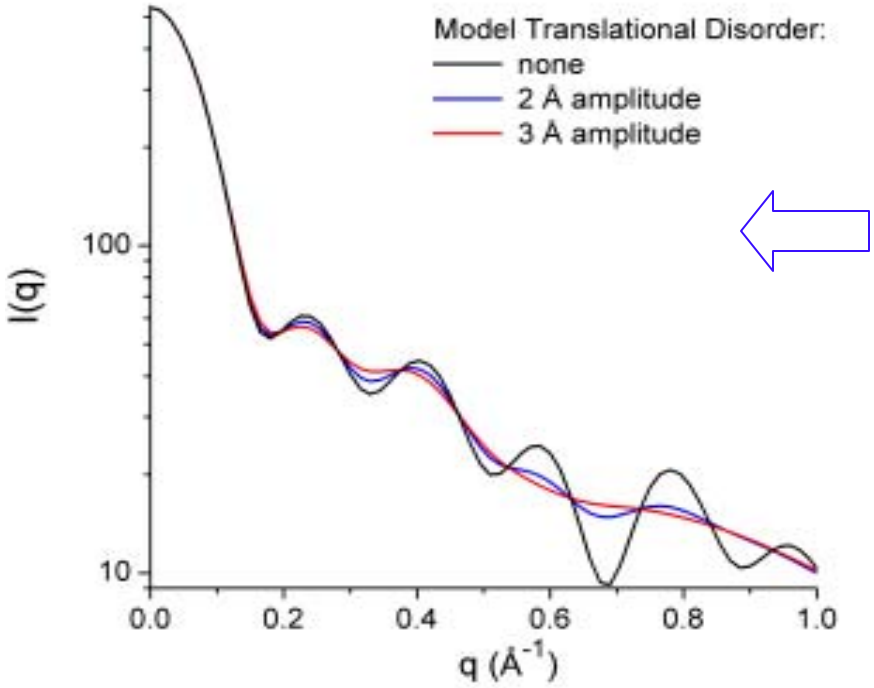
7.8 Å Resolution XS Data :

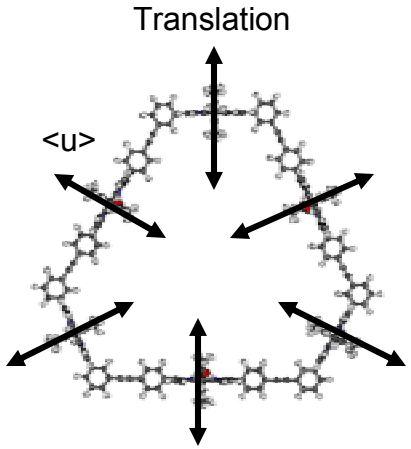
- **Resolved Porphyrin PDF:**
  - **•Cyclic Structure**
- **Host PDF Peak 1.5 Å Shorter than Model**
- **Insert Guest: Slight (0.6 Å) Expansion**
  - **•Exp ~ Model**
- **Major Differences PDF Width/Dispersion**
- **Host-Guest Narrower Dispersion**

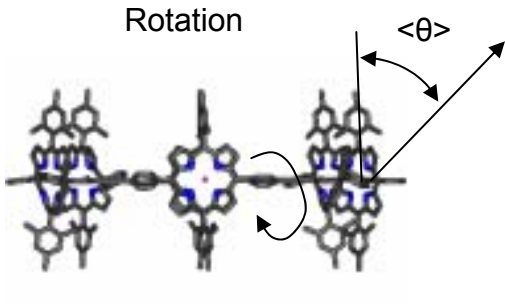


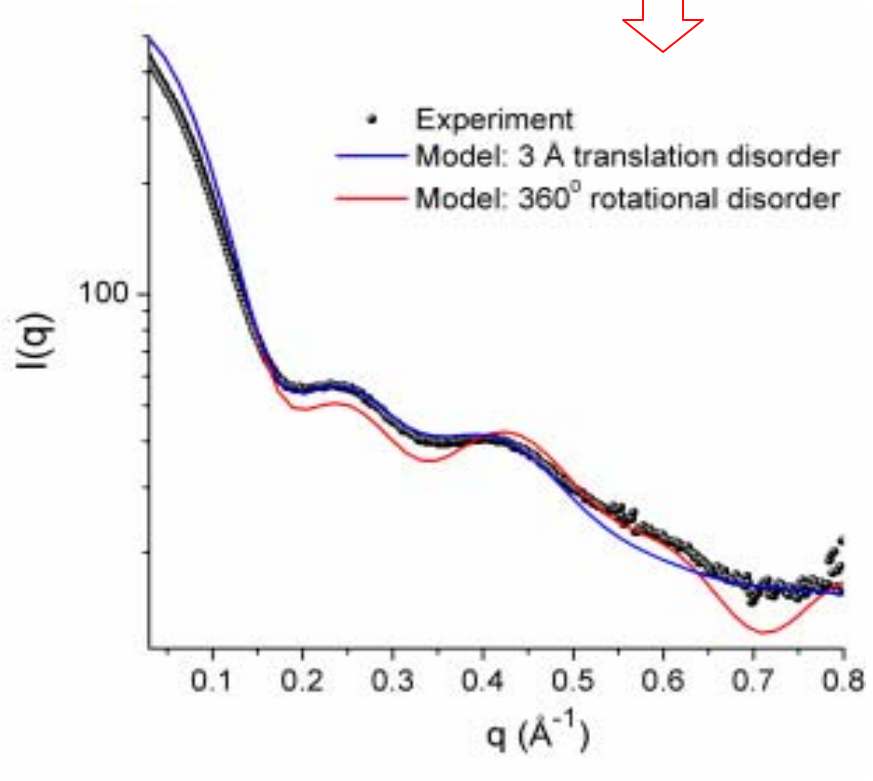
Damping of Porphyrin Wheel Diffraction by Rigid-Body Motion

Ruitian Zhang









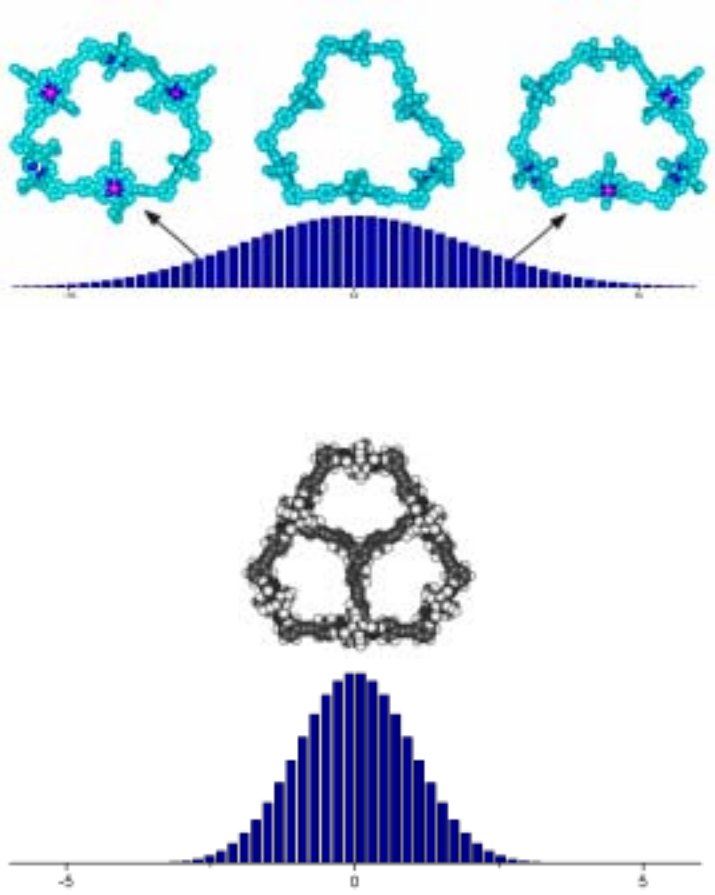
Damping of Molecular Diffraction
Measure Configurational Dispersion

Data Allows
- Up to 3 Å Translational Disorder
- Full Rotational Disorder
- Defines Conformational Envelope

Solution Diffraction of Cyclic Porphyrin Architectures

Measured Solution Structure:

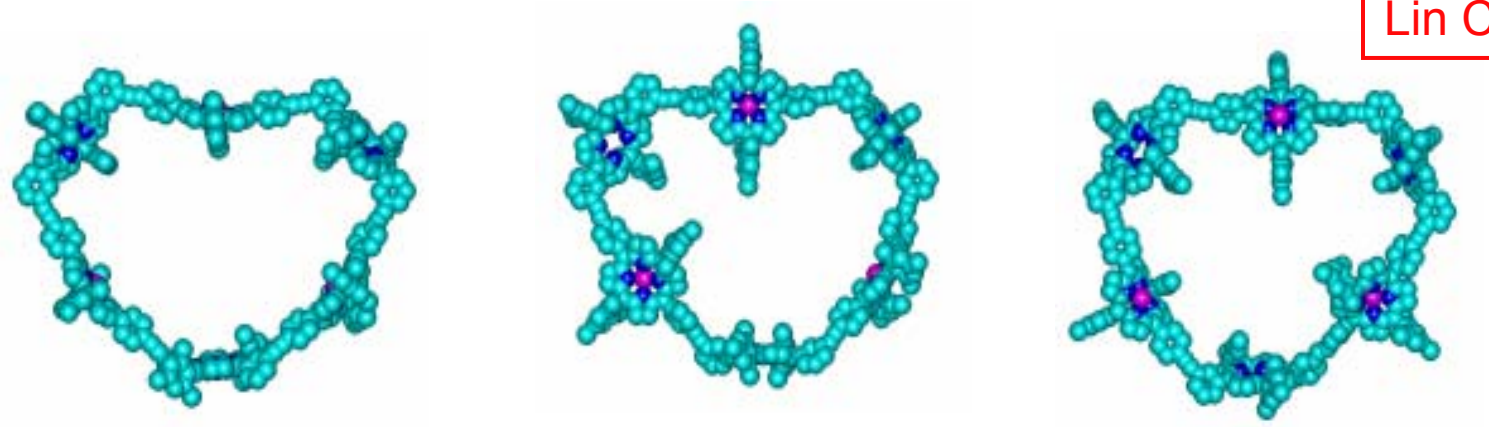
- **Molecular architecture**
  - Characteristic PDF = Cyclic Architecture
- **Equilibrium Conformation**
  - Host Array Centered on 1.5 Å Shortened “Puckered’ Conformation
  - Host-Guest Array Expanded, Close to Model Conformer
- **Configurational Envelope: Amplitude of Configuration Dispersion**
  - Host Array “Floppy”:
    - < 3 Å translational dispersion,
    - Full rotational dispersion
  - Host-Guest ~2x Smaller Dispersion



Connection:
Molecular Diffraction Amplitudes-Conformational Dispersion

Snapshots of individual conformers within a 1ns MD Simulation:

Lin Chen



MD Numerical Model:
Porphyrin/Linker Bowing
Porphyrin Group Rotation

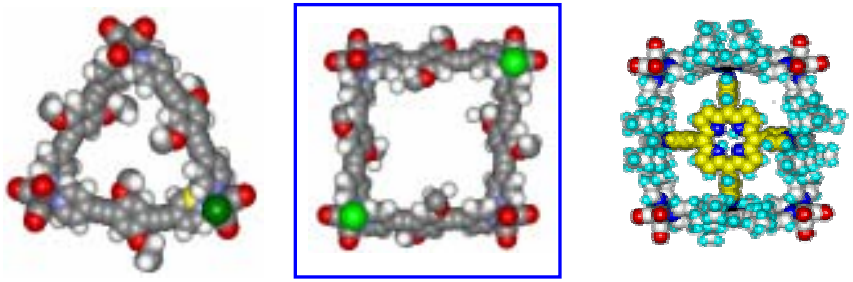
Rigid-Body Analytical Approximation :
Porphyrin Group Translation
Porphyrin Group Rotation

New Opportunity-
Measure Conformational Dispersion for Molecules in Solution:

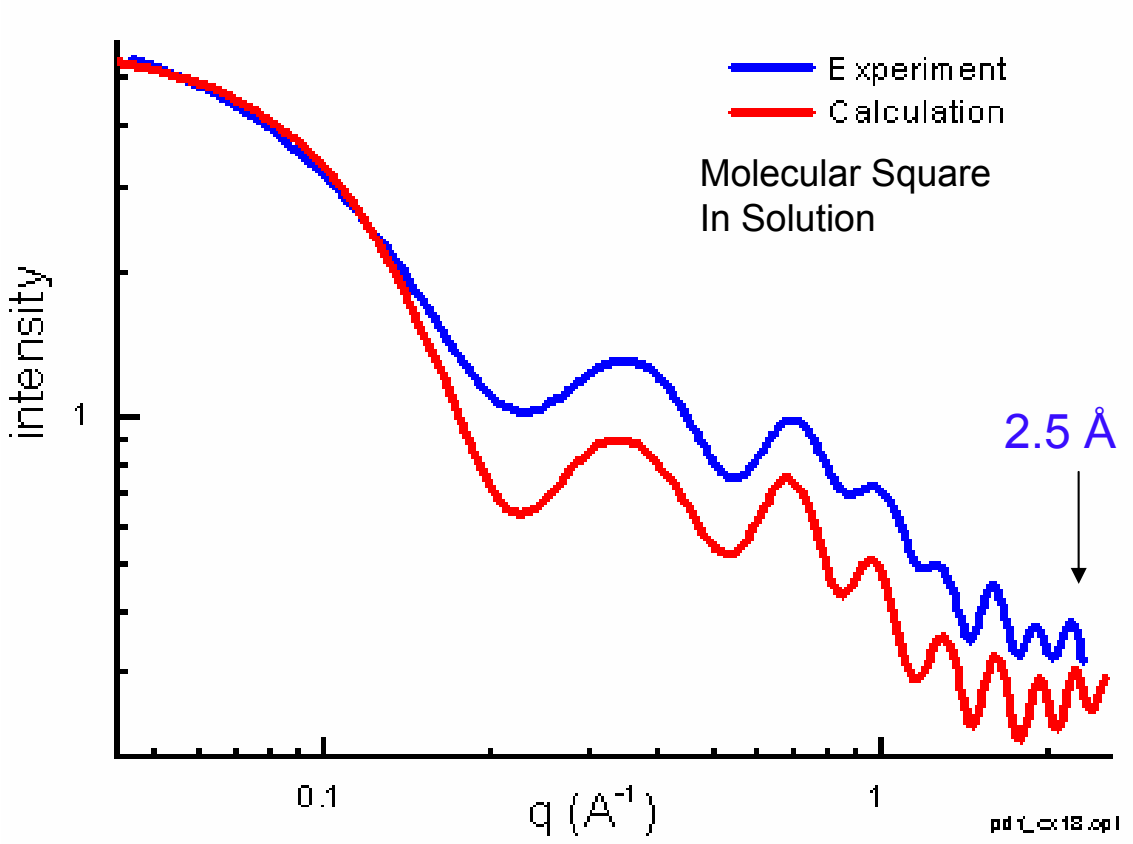
- Paramertize dampening in terms rigid-body motions
- Quantitative comparison to MD:
  - Calculate scattering for conformational ensemble

Supramolecular Architectures based on Coordination Chemistry

Joseph Hupp, Northwestern University



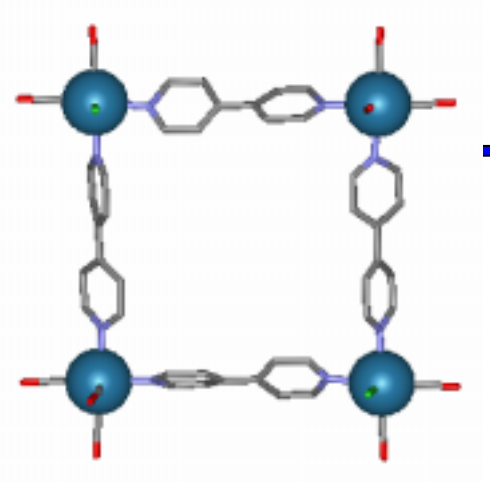
Building Blocks:
> photochemistry/conversion
> catalysis
> photonics
> separations



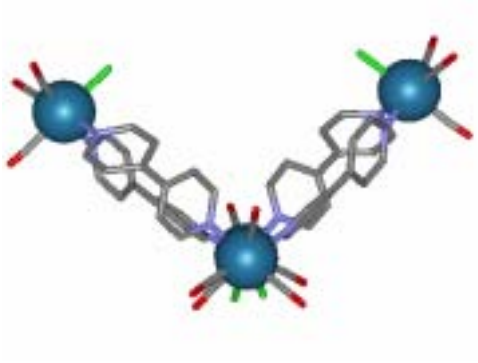
- Exp Scattering Amplitudes Comparable to Calc
- Homogeneous, Rigid Assemblies
- Exp Scattering Amplitudes Not Instrumentally Limited

Bipyridyl Squares: Comparison to Models

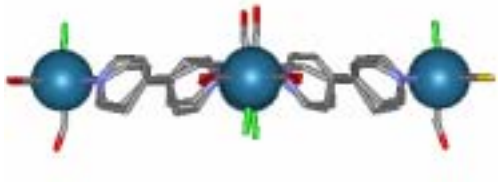
Jodi O'Donnell



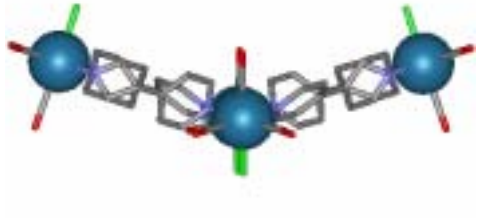
Crystal: Puckered

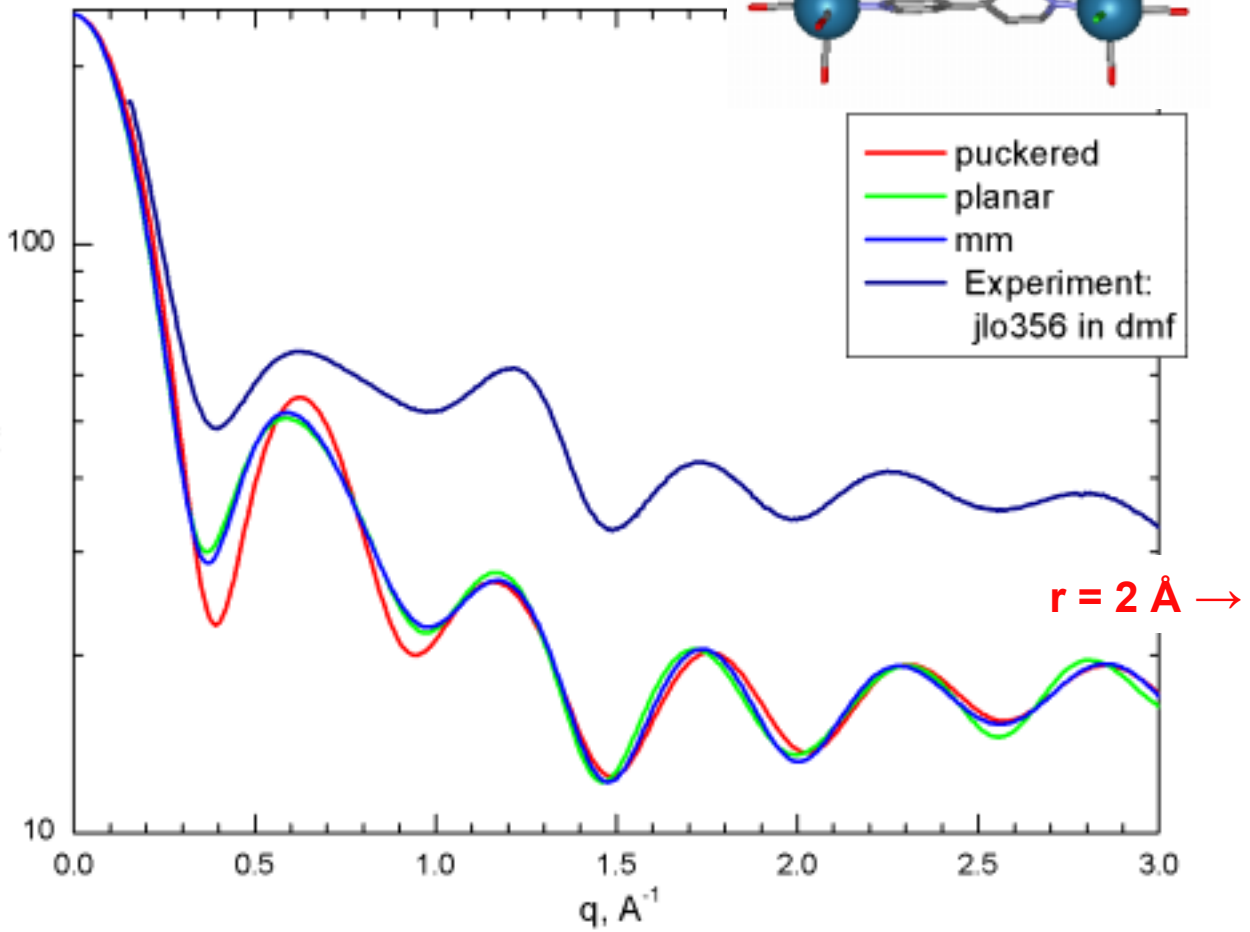


Crystal: Planar



Energy Minimized Model





High-resolution diffraction with configurationally constrained molecules

_18june2003_data

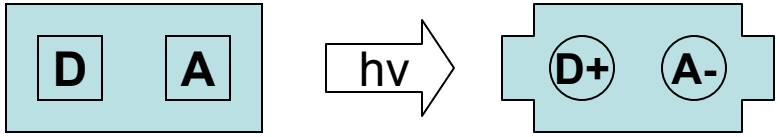
Supramolecular Diffraction in Solution

Measure of Structure in Solution :

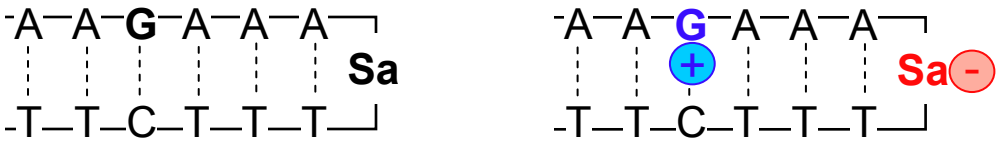
- **Equilibrium Conformation**
- **Conformational Dispersion**
- **Solvent Packing, Structure Molecular/Solvent Interface, Site-Specific vdw Volumes**
- **Time-Resolved, Reaction-linked Structural Change**

Time-Resolved, Reaction-linked Structure Change

(work in progress)



DNA



F. Lewis
X. Zuo

M. Wasielewski

Model, well-defined matrix for ET

Reaction Centers

Nano Hybrids

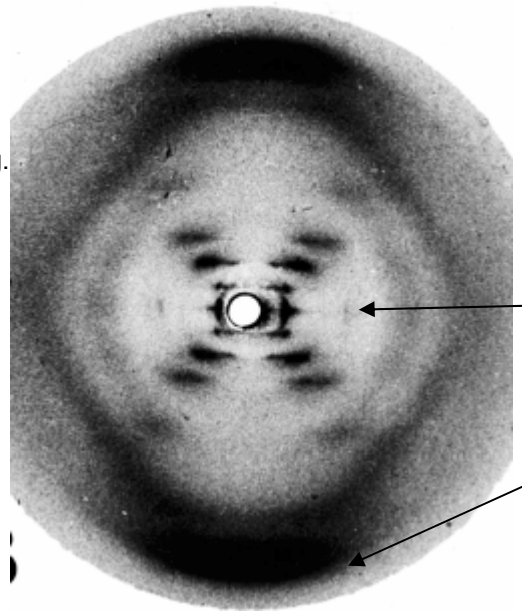
T. Rajh
N. Dimitrijevic
P. Zapol

DNA Molecular Diffraction

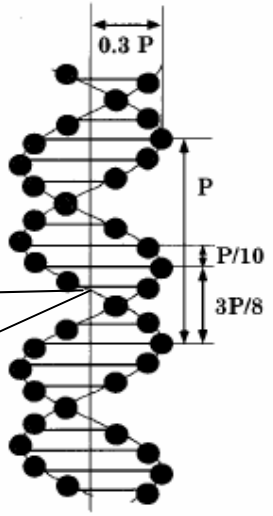
Xiaobing Zuo

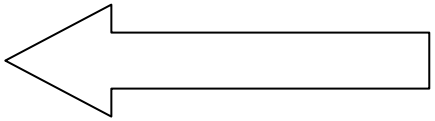
Fiber Diffraction

Franklin and Gosling, Acta Crystallog. 1953, **6**:673



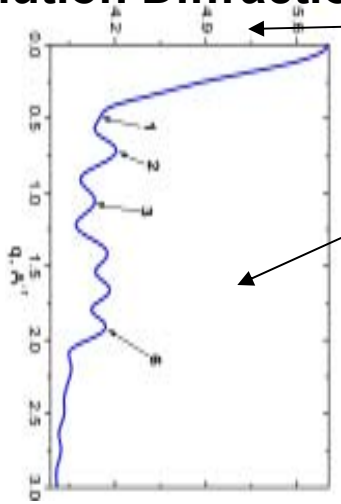
DNA Structure

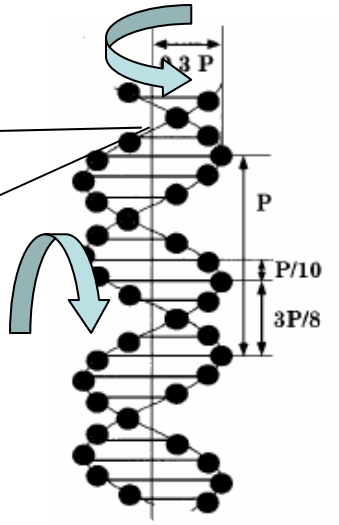


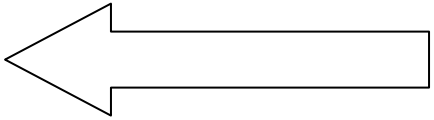


Solution Diffraction

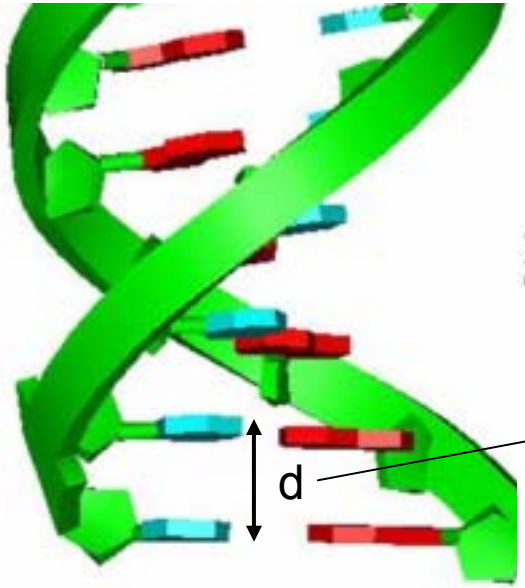
Zuo, Lewis, Tiede, Airlie House, 2004



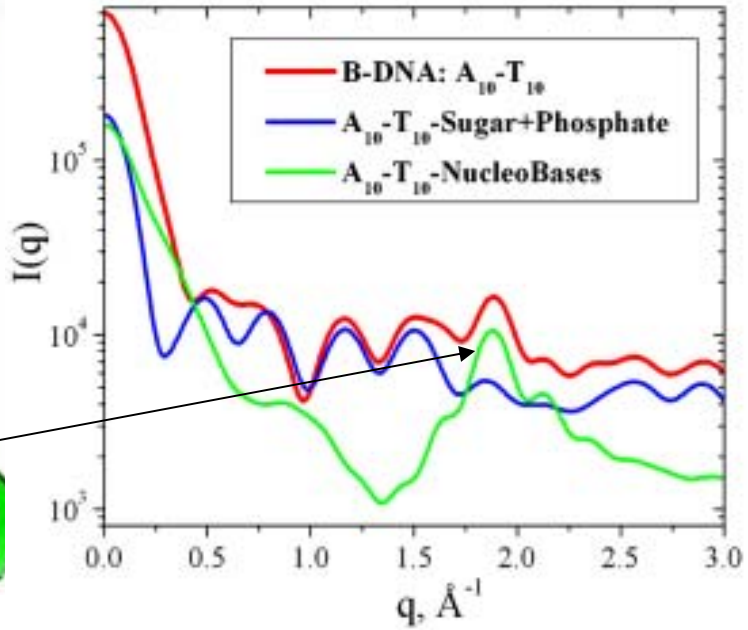


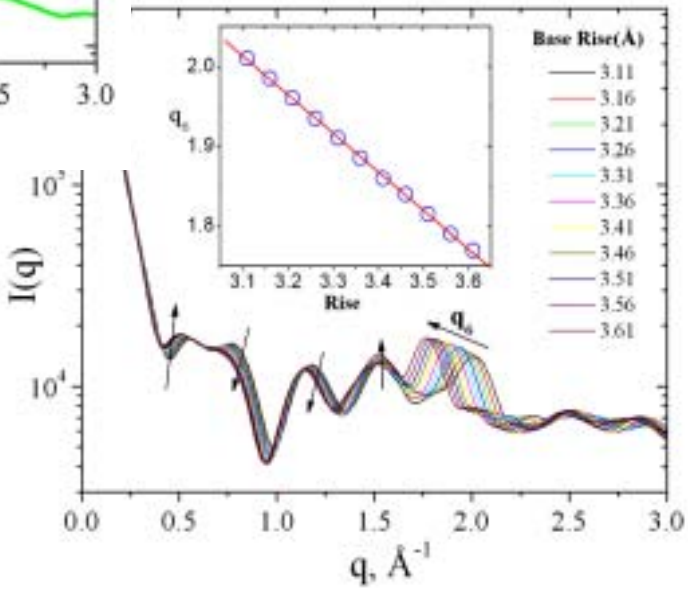


General Characters of DNA Molecular Diffraction



Base Rise

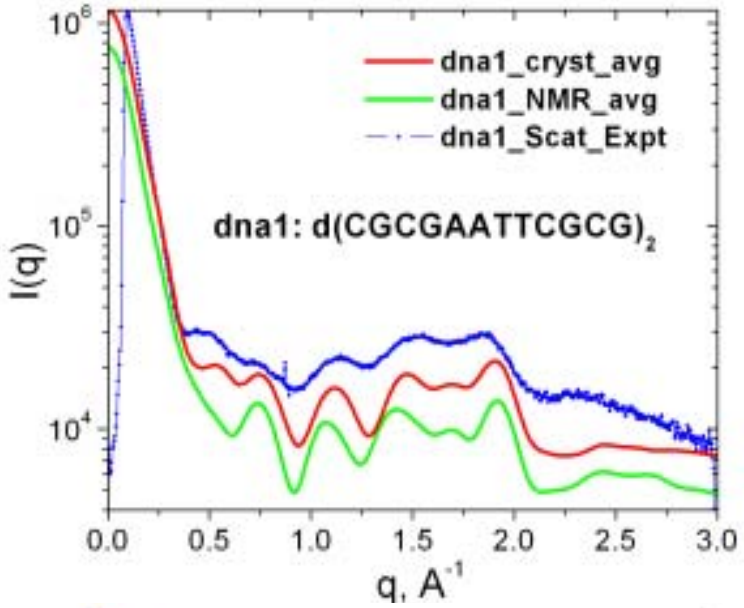




Separation of π-stacked bases potentially significant for molecular wire properties

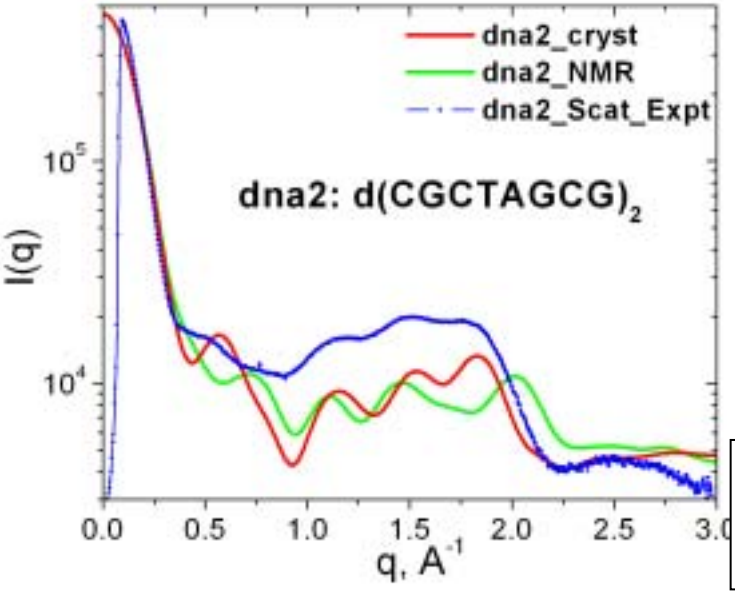
DNA Structure in Crystal & Solution:

Dickerson DNA



dna1:
CGCGAATTCGCG

cryst. model: bdl001
NMR model: 1duf

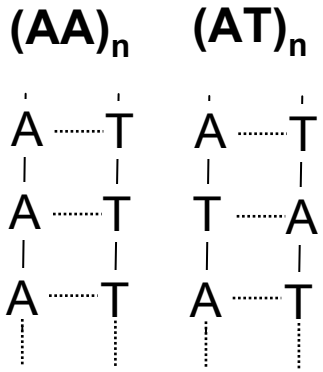


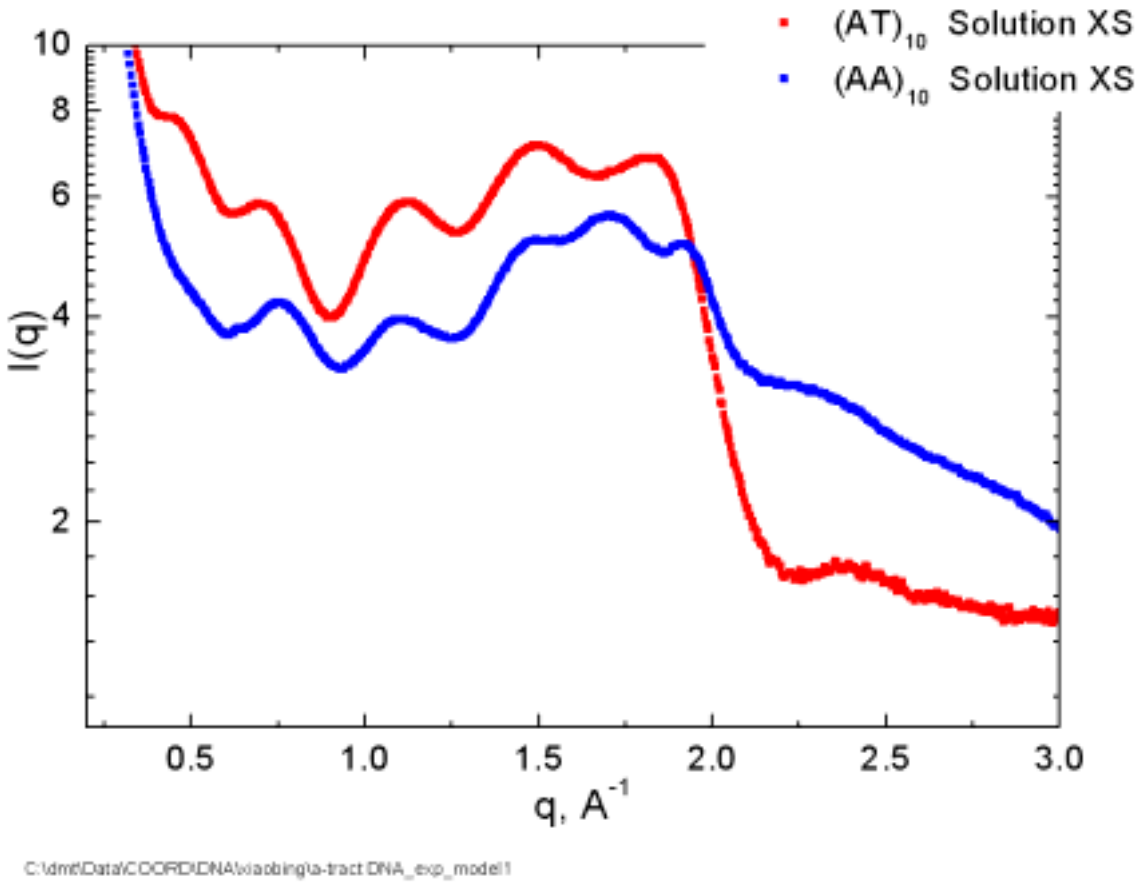
dna2:
CGCTAGCG

cryst. model: 250d
NMR model: 1q7z

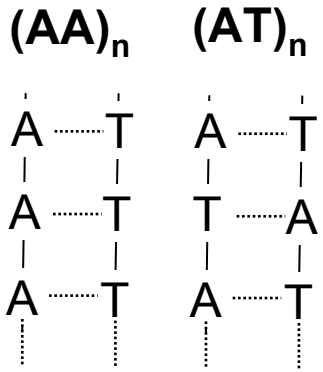
Sequence Matters-
For details of structure/dynamics

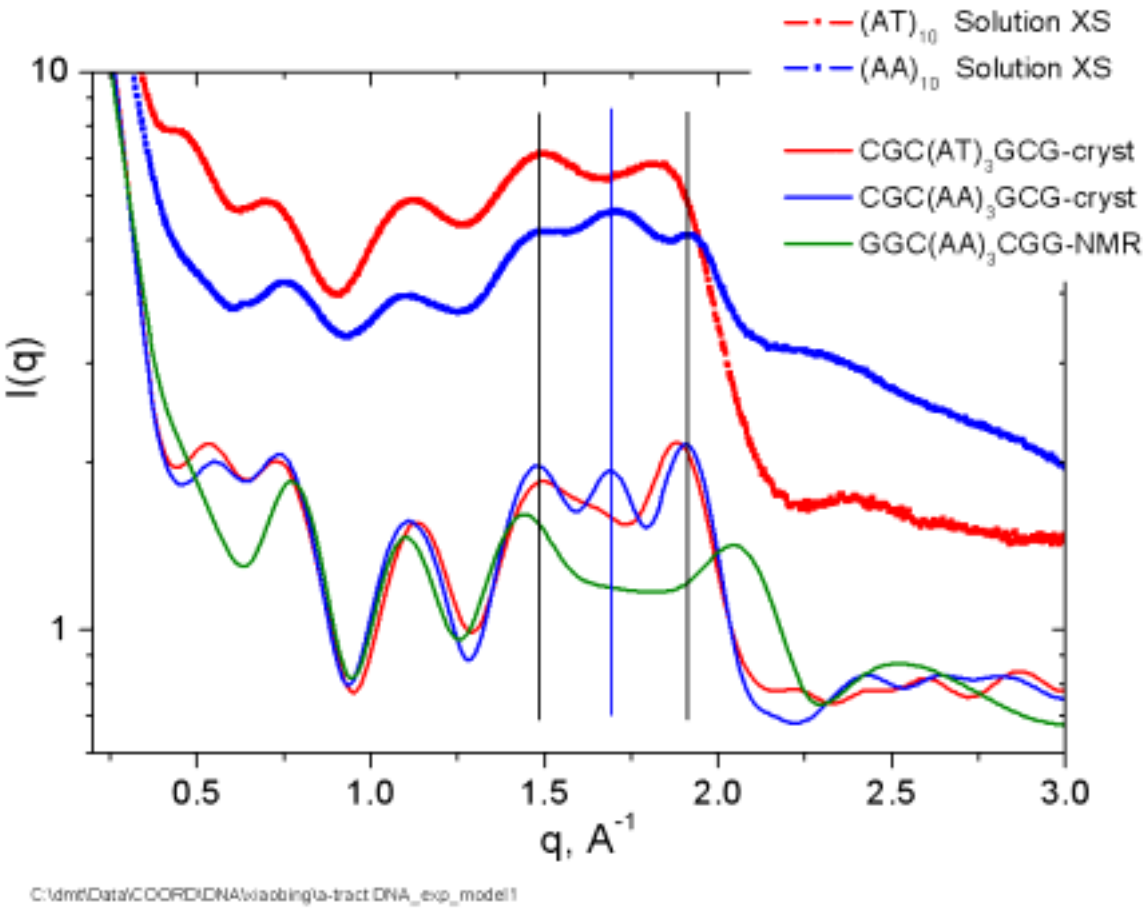
ET Spacer Sequences: $(AA)_n$ vs $(AT)_n$





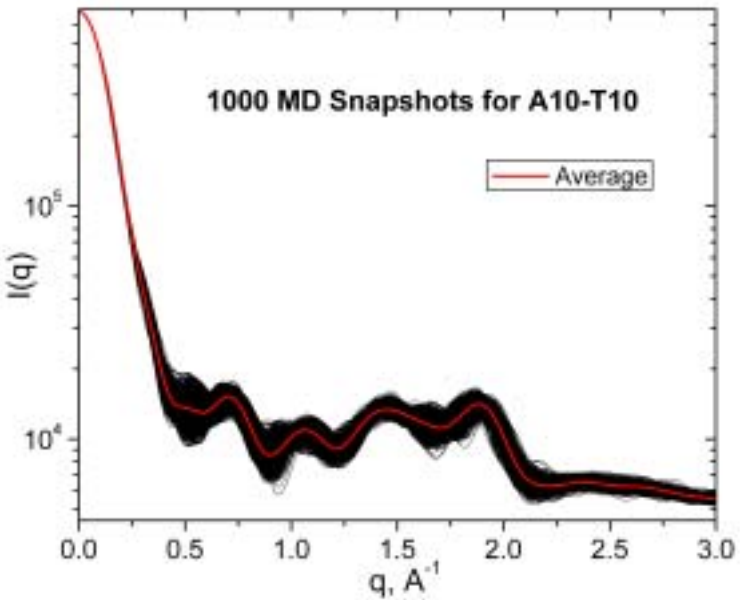
ET Spacer Sequences: $(AA)_n$ vs $(AT)_n$: Comparison to Crystallographic and NMR Models

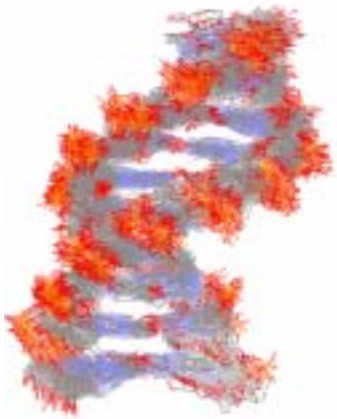




- Distinguish crystallographic and NMR models
- Evaluate applicability to solution state

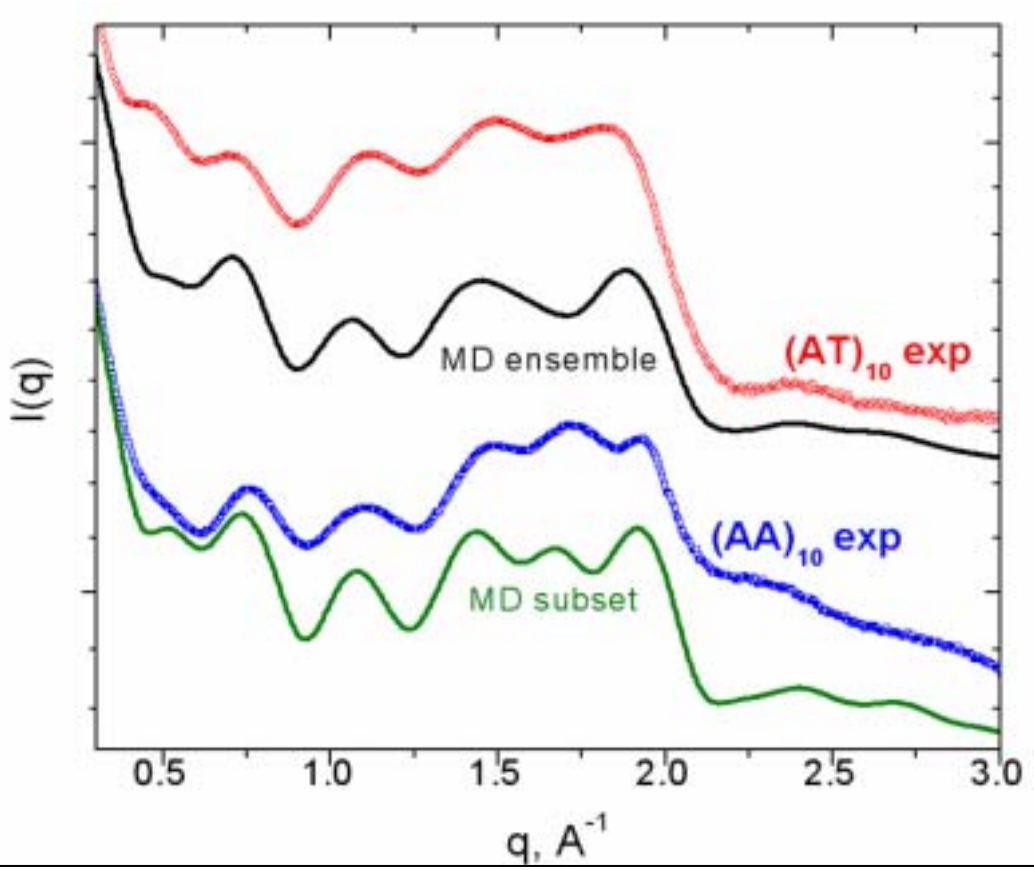
ET Spacer Sequences: $(AA)_n$ vs $(AT)_n$: Comparison to MD Ensembles





2ns Amber
$(AA)_5$
$(AA)_{10}$ $(AT)_{10}$

Xiaobing Zuo
P. Zapol
Guanglei Cui
K. Merz



- MD ensembles good match for $(AT)_n$ *not* $(AA)_n$
- MD force-field skewed to $(AT)_n$ conformation
- $(AA)_n$ conformers found in MD sub-sets
- Experimental guide to refine force-field

Supramolecular Diffraction in Solution

Coordinate-based Comparison of Molecular Models :

- **Crystal**
- **NMR**
- **MD**
- **Time-Resolved, Reaction-linked Structural Change**

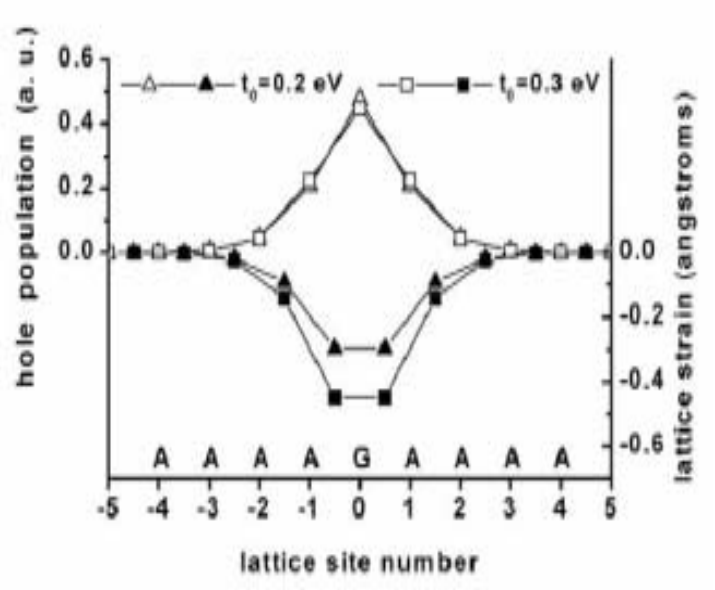
MM Prediction of Hole-injection Structural Change

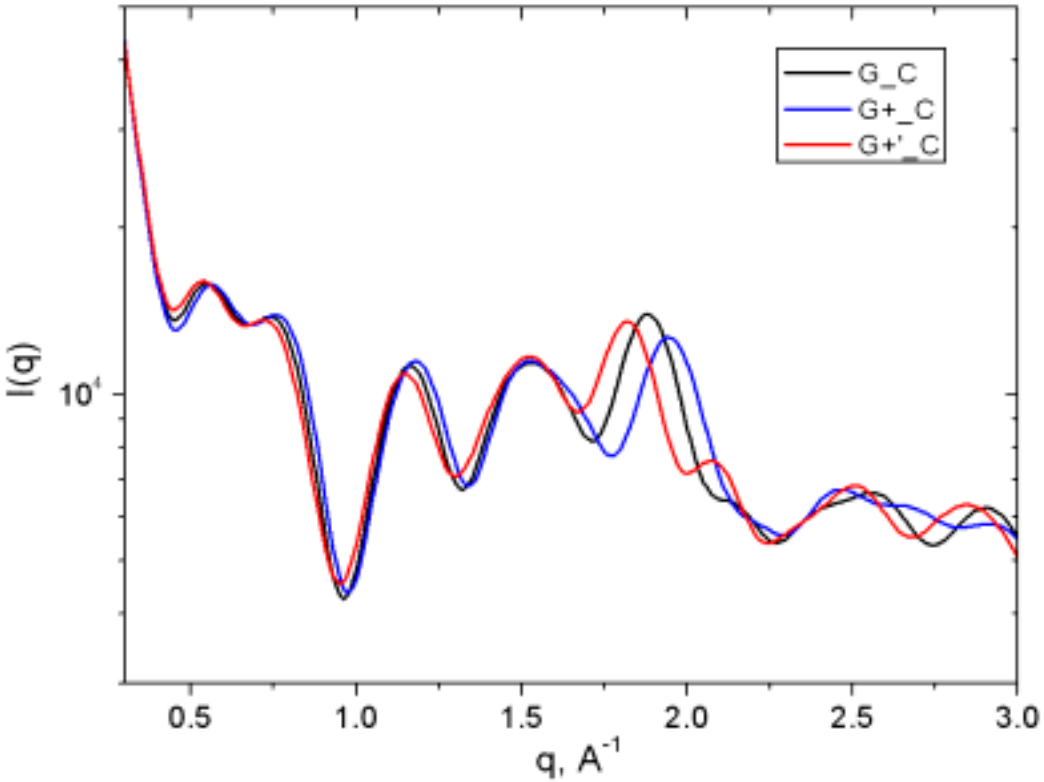
A A A A G A A A A
T T T T C T T T T

A A A A **G** A A A A
+
T T T T C T T T T

Xiaobing Zuo

Conwell, Esther:
Top. Curr. Chem. (**2004**) *237*:73–101



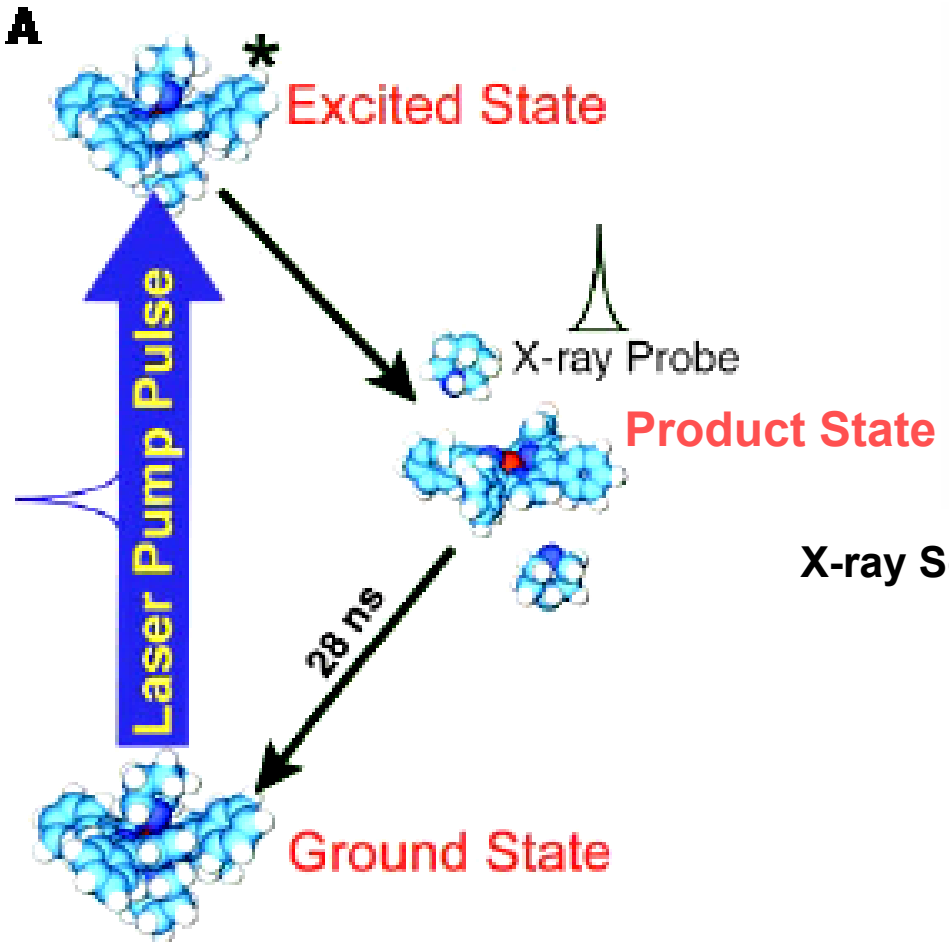


Solution Molecular Diffraction Experiments Have Sensitivity to Detect Predicted Structure (lattice strain) Change

New Opportunities for Time-Resolved Structure Analyses Using Laser Pump-Synchrotron Probe

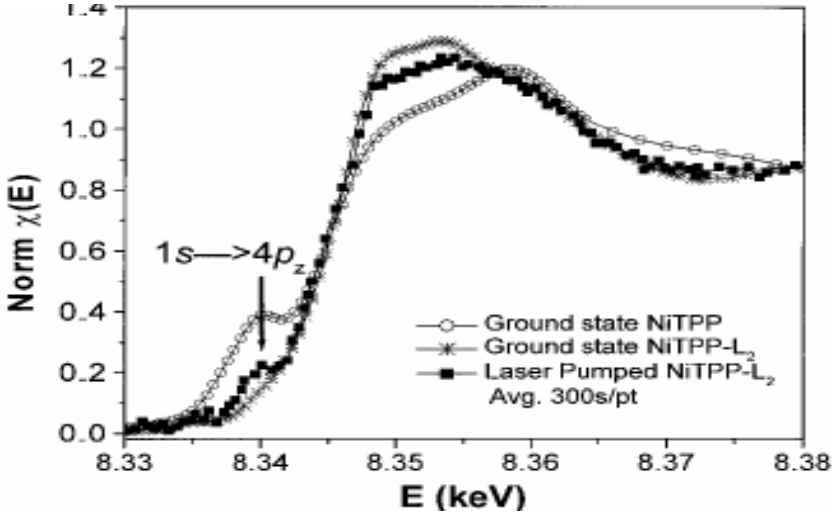
Lin Chen

Transient Porphyrin Photochemistry:

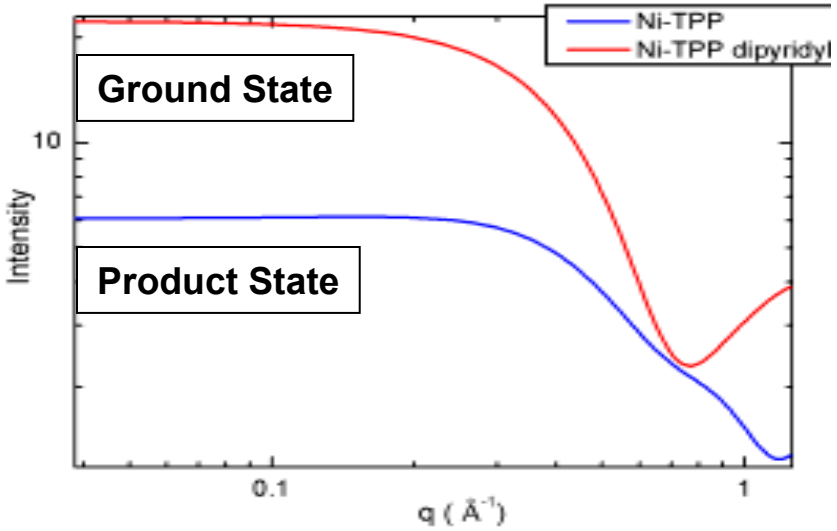


XAFS Experiment:

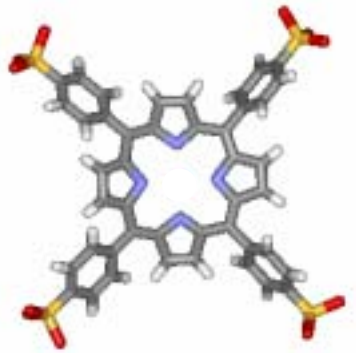
(**Lin Chen** et. al. 2001 Science 292:262)



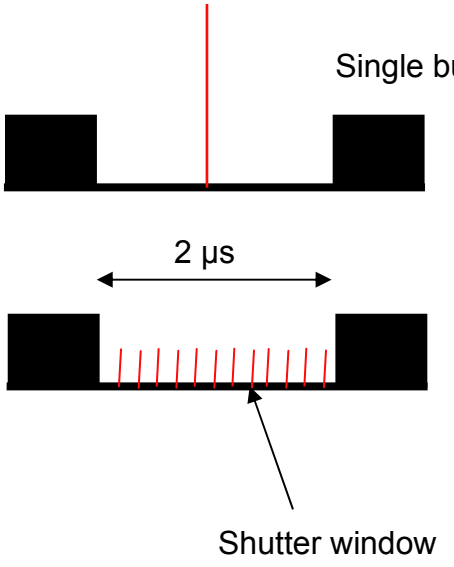
X-ray Scattering Experiment:

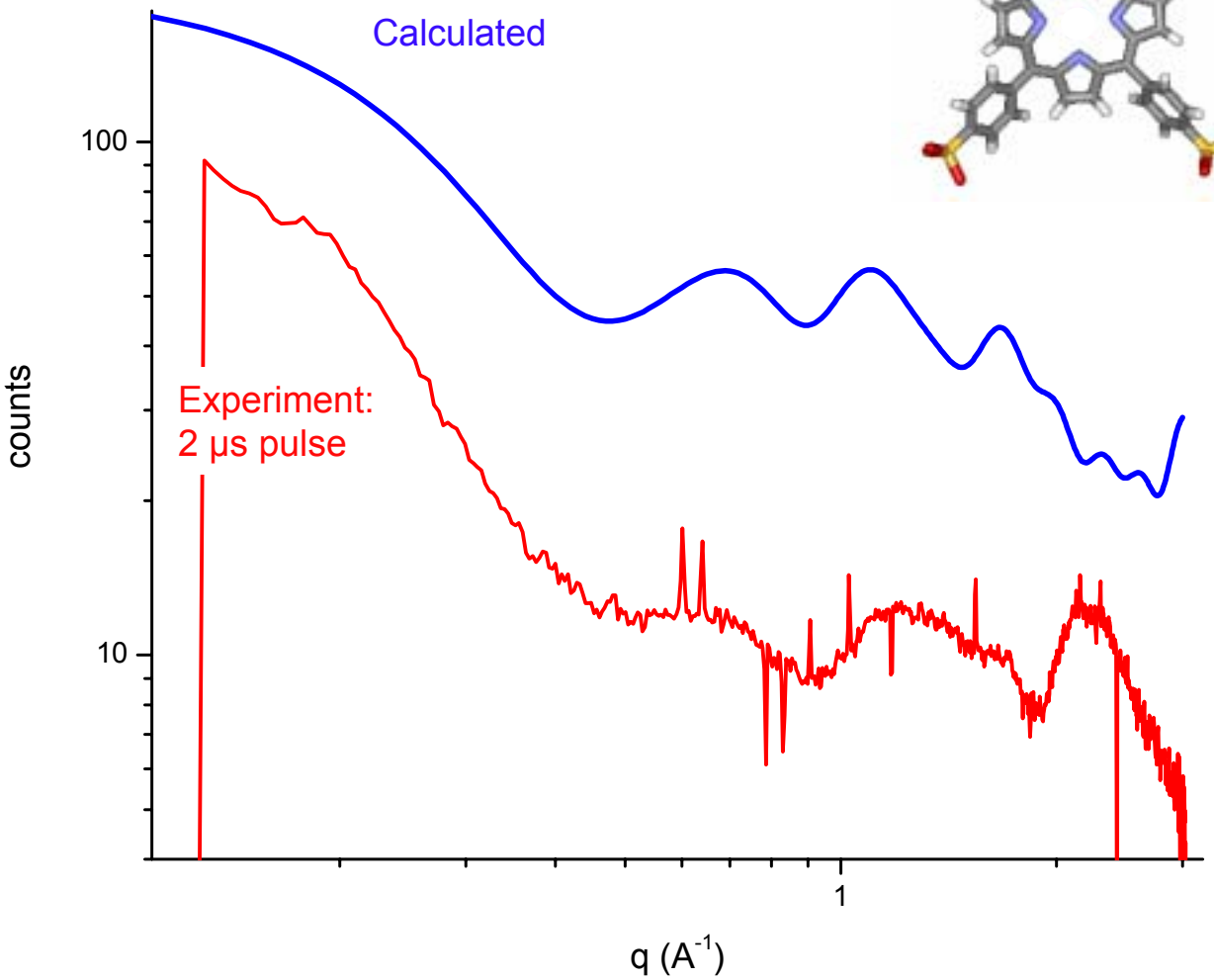


Time-Resolved, Molecular Diffraction Measurements

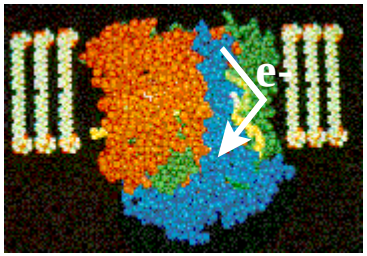


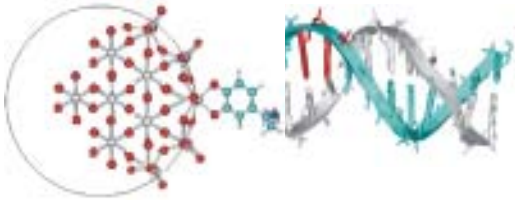
APS Timing Modes:





Acknowledgements





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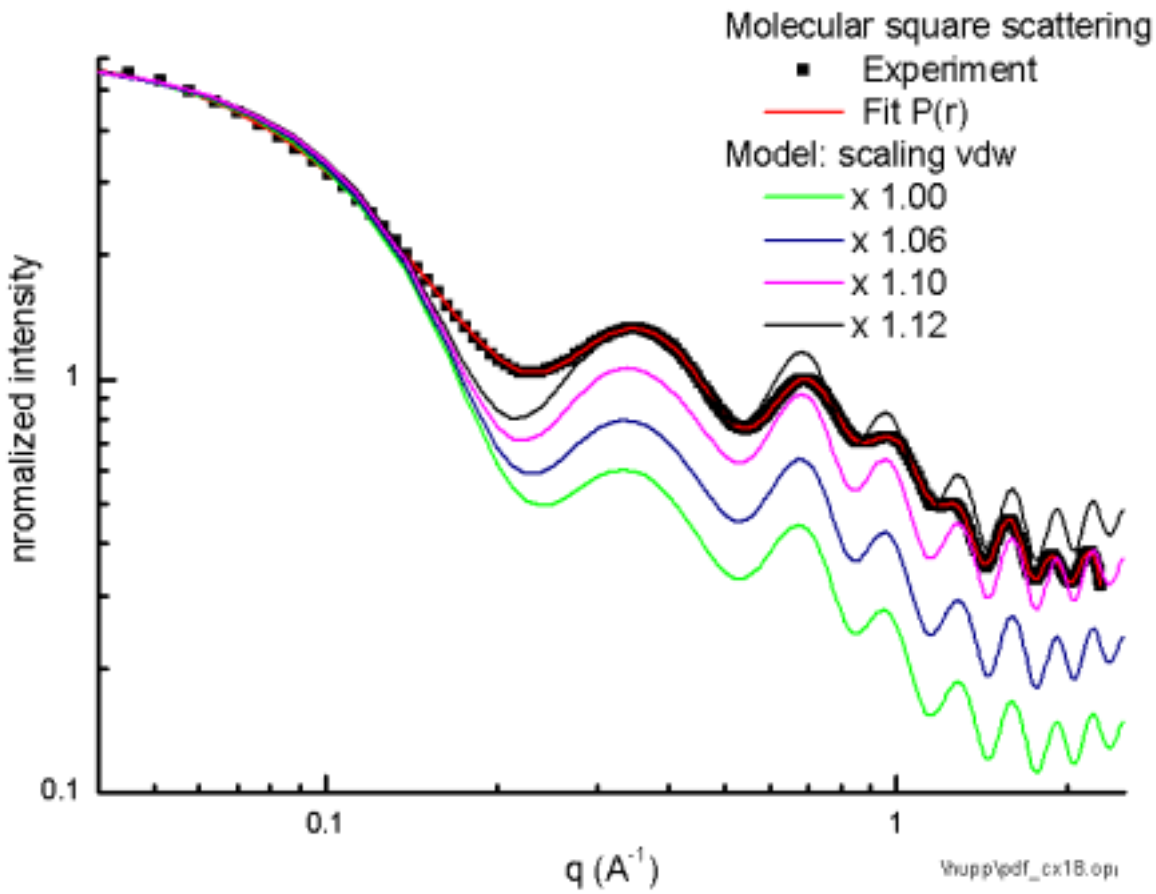
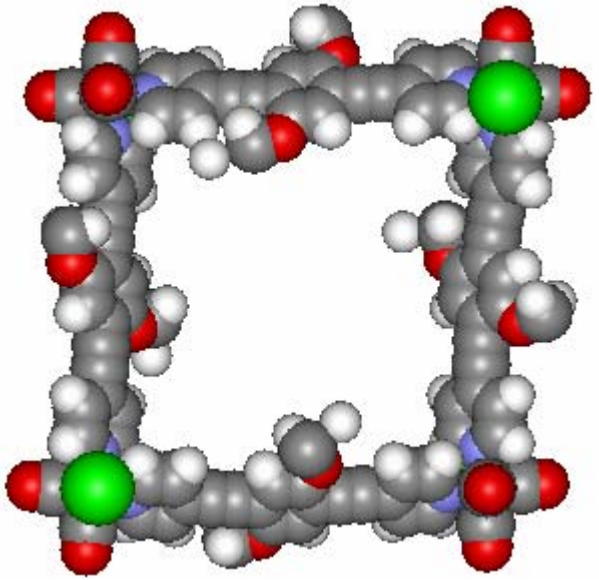
Effect of Scaling vdw Volumes on Calculated Scattering



Model:

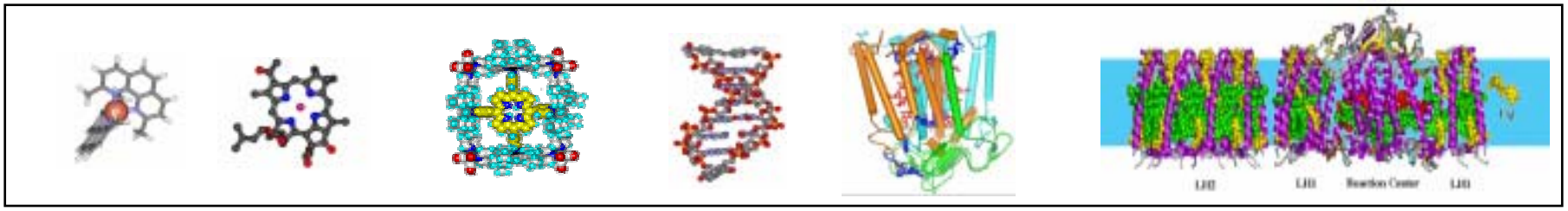


- Atomic vdw Volumes Affect Scattering via “Contrast”, Scattering Amplitudes
- Atomic vdw Effect Distinguishable Dynamic Effects
- Detailed Modeling Opportunity to Identify “Site-Specific” Solvent Packing

High-Angle X-ray Scattering

New Opportunity to Quantitatively Explore Molecular Structure In Liquids:

- **Molecular architecture and conformation**
  Quantitative test of crystal, NMR, or other coordinate models
- **Dynamics**
  Quantitative tests of MD simulations
- **Solvent Packing, Structure Molecular/Solvent Interface, Site-Specific vdw Volumes**
  Especially, with small, conformationally restricted assemblies: significant for understanding chemistry
- **Time-resolved, Reaction-Linked Structure Re-organization**



Modeling Effect of Rigid-Body Motions on Wide-Angle X-ray Scattering

Break Macromolecule into Fragments:

$$I(q) = \left\langle A(\mathbf{q})\, A(\mathbf{q})^{*} \right\rangle = \left\langle A_1(\mathbf{q})^2 + A_2(\mathbf{q})^2 + 2\, A_1(\mathbf{q})\, A_2(\mathbf{q}) \right\rangle$$

$$A(\mathbf{q}) = \sum_j f_j(q) e^{i\mathbf{q}\cdot\mathbf{r}_j}$$

Introduce Fragment Thermal Factor:

(Zhang et al. (1999) Langmuir 15:7510 ; Tiede et al. JACS submitted)

$$I(q) = \left\langle A_1(\mathbf{q})^2 + A_2(\mathbf{q})^2 + 2\, A_1(\mathbf{q})\, A_2(\mathbf{q}) e^{-u^2 q^2} \right\rangle$$

Weighting describes coherence in fragment positions in terms rms amplitude, u